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BINARY NICKEL ALLOY PHASE DIAGRAMS COMPILATION AND CRITICAL EVALUATION

Status Report for the period
June 1982 - February 1983

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During the early part of the reporting period, Dr. Philip Nash, category editor and principal investigator for evaluating the binary nickel alloy phase diagram systems, prepared a computer program to format data for input to the optimization program of Henig and Lukas. The computer program efficiently aids extraction and input of data from the literature.

Subsequently evaluations for the molybdenum-nickel (Mo-Ni), nickel-vanadium (Ni-V), hafnium-nickel (Hf-Ni) and nickel-zirconium (Ni-Zr) systems were completed and submitted for review. Evaluation work is in progress for the nickel-aluminum (Ni-Al), nickel-copper (Ni-Cu), and nickel-chromium (Ni-Cr) systems. As an example of work being accomplished, Attachment A to this report is the evaluation for the Hf-Ni system. This evaluation is subject to review and alteration.

To maintain an efficient schedule, the principal investigator has determined that it is necessary to have a number of on-going evaluations because of the time involved in obtaining obscure references, in obtaining all references for certain systems for which there are a large number of publications, and in interacting with investigators who are evaluating other specific elements alloyed with nickel.

Prepared by James Hontas

KRoman/T12
16 March 1983

Attachment A
Subject to review
and alteration

The Hf-Ni System

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Equilibrium Diagram

General Features

The Hf-Ni equilibrium diagram based mostly on the work of 79BSE and 67SVE is shown in Figure 1. The system is quite complex due to the number of intermediate phases formed. The general features of the diagram are the nine intermediate phases, two of which Ni_7Hf_2 and NiHf are congruently melting whilst the other seven are formed peritectically, the very limited terminal solid solutions and the metatectic reaction involving the allotropic transformation in Hf. Since no information is available regarding solubility in the intermediate phases these have been taken to be line compounds. A recent review of this system by 81NAS omits the metatectic reaction.

It should be noted that the Hf used in all of the experimental studies contained zirconium, in some cases as much as 3 wt % Zr. Generally, authors have not worried about this as the Ni-Zr system is considered to be very similar to Ni-Hf, however, the addition of Zr to Hf lowers

its melting point and this will probably have an effect on the Ni-Hf diagram with the greatest effect being at the Hf rich end. In addition, the possibilities of contamination due to oxygen have never been addressed.

Intermediate Phases

There has been some confusion over the number of intermediate phases caused partly by alternative designations for the same phase and partly by contradictory evidence concerning the existence of certain phases. However, those shown in Figure 1 and listed in Table 1 are fairly well established.

A very limited study of this system by 61KIR1 using metallographic and x-ray experiments found the system to be analogous with Ni-Zr with 7 compounds designated $NiHf_2$, NiHf, $Ni_{11}Hf_9$, $Ni_{10}Hf_7$, NI_5Hf, Ni_5Hf_2 and Ni_7Hf_2. Another limited study by 61DEA found 5 compounds, $NiHf_2$, NiHf, Ni_3Hf_2, Ni_2Hf and Ni_4Hf and a depression of the hafnium transition temperature on addition of Nickel with the transition occurring above the Hf + $NiHf_2$ eutectic giving a metatectic reaction. This work was not published other than as an internal report as the author had insufficient confidence in the results. An extensive study of the system by 67SVE using thermal, microscopic and x-ray techniques revealed the existence of 5 compounds designated $NiHf_2$, NiHf, $Ni_{11}Hf_9$, Ni_3Hf_2, Ni_5Hf_2, Ni_3Hf, Ni_7Hf_2 and Ni_5Hf. In

addition, they determined the solidus and liquidus and confirmed the presence of a metatectic reaction β(Hf)→ α(Hf) + L. Thus the existence of the phases $NiHf_2$ and NiHf has been established having been found in three independent investigations. The compound designated $Ni_3Hf_2$by 67SVE and 61DEA is the same as the $Ni_{10}Hf_7$ phase found by 61KIR1. Further independent work has confirmed the existence of the phases Ni_5Hf 61DWI, Ni_7Hf_2 73DAT and 79BSE and Ni_3Hf 79BSE which has two polymorphs.

The existence of an $MgCu_2$ type Laves phase has not been clearly established. 72PET and 73KOC claim the existence of the phase Ni_2Hf on the basis of x-ray, microprobe and thermal arrest data. 54ELL on the basis of x-ray diffraction data from an alloy of Ni -33 at. % Hf concluded there was no obvious similarity to a Laves type pattern. 79BSE suggests that such a phase is stabilized by silicon contamination from the silica tubes in which the alloys are equilibrated. However, both 72PET and 73KOC note the presence of the $NiHf_2$ phase in 'as cast' alloys prior to any heat treatments. Thus the formatiion of Ni_2Hf may be promoted by some other impurities such as oxygen. Both the microprobe and thermal arrest data of 72PET and 73KOC can be interpreted without involving an Ni_2Hf phase but using the Ni_7Hf_3 phase found by 79BSE. The complexity of this region of the diagram means that it is not amenable to

determination by use of dynamic methods such as thermal analysis.

Recently the central portion of the diagram has been studied by 79BSE with the result that a phase Ni_7Hf_3 was found to exist with a limited range of stability from $1250\pm20^{o}C$ to $1016\pm3^{o}C$ at which temperature the phase decomposes into $Ni_{10}Hf_7$ and Ni_3Hf (β). On the basis of crystal structure determination 79BSE has designated the phase Ni_5Hf found in previous work as $Ni_{21}Hf_8$. The stability range is from $1300\pm20^{o}C$ where $Ni_{21}Hf_8$ forms peritectically from liquid and Ni_3Hf down to $1175\pm10^{o}C$ where it decomposes eutectoidally into Ni_7Hf_3 and Ni_3Hf (β). The Ni_3Hf phase was found to form peritectically at $1350\pm20^{o}C$ from liquid and Ni_7Hf_2 and to undergo a polymorphic transition at $1200\pm10^{o}C$.

67SVE obtained thermal arrests in the solid state around the composition NiHf which they attributed to a polymorphic transition in that compound. They also determined the congruent melting temperature of NiHf and Ni_7Hf_2 as $1350^{o}C$ and $1480^{o}C$ respectively.

Liquidus and Solidus

The only data available on the liquidus is from 67SVE determined by thermal arrest measurements. 54ELL reports the incipient melting temperature of an Ni_2Hf alloy as $1790^{o}C$ which cannot be reconciled with the liquidus data of

67SVE as it is approximately 540°C higher. The incipient melting temperature was probably determined by observing the change in angularity of a specimen suspended in a vacuum furnace as described by 52HAN. Since Hf is highly reactive Ni-Hf alloys readily form a tenacious oxide layer even in a vacuum which is probably capable of maintaining the specimen geometry even when the alloy itself is molten. The data for the liquidus have, therefore, been taken only from 67SVE.

The peritectic reactions have been determined by 67SVE and 79BSE as already discussed with confirmation of the reactions for $NI_{10}Hf_7$, $Ni_{21}Hf_8$ and Ni_5Hf from 61KIR1. The L→(Ni) + Ni_5Hf eutectic composition was determined as 88 at % Ni at 1190°C by 67SVE. The L→ Ni_7Hf_3 + $Ni_{10}Hf_7$ eutectic was determined as 63 at % Ni at 1200°C by 67SVE, as 65 at % Ni at 1190±10°C by 79BSE and around 64 at % Ni by 61KIR1. The two other eutectics found by 67SVE are supported by 61KIR who found the composition of L→ α (Hf) + $NiHf_2$ to be around 75 at. % Ni and the composition of the L→ Ni + Ni_5Hf eutectic to be around 89 at % Ni. 61KIR1 suggest that the compound $NiHf_2$ is congruent melting analogous with its zirconium counterpart and that there is an associated eutectic L→ NiHf + $NiHf_2$ around 25 at % Ni. The more extensive work of 67SVE has been preferred and the phase $NiHf_2$ taken as forming peritectically from the melt and NiHf.

Terminal Solid Solutions

Although little data is available on the temperature variation of solid solubility of Hf in Ni and Ni in Hf it is clear that they are very restricted. 60REI found a maximum solubility of 0.7 at. % Hf in Ni at approximately 1200°C whilst 67SVE state that the solubility of Hf in Ni is 1 at % at 1050°C, however, their data point appears at 1150°C on their phase diagram. 72KAU found the solubility of Hf in Ni to be less than 0.2 at. % at room temperature on the basis of ion implantation studies. In Fig. 1, the maximum solubility of Hf in Ni has been taken to be 1 at. % Hf at 1190°C.

Metastable Phases

Buschow and Beekmans (79BUS) prepared $Hf_{1-\chi}Ni_{\chi}$ amorphous alloys by arc melting followed by melt spinning in an atmosphere of purified argon for the concentration range $0.2 \leq \chi \leq 0.89$. X-ray diffraction patterns of the as melt spun ribbon showed amorphous structures. The crystallization temperatures were determined by means of differential scanning calorimetry. Their Results were as follows:

1. $Hf_{80}Ni_{20}$: Three transformations were found to occur at 465°C, 525°C and 630°C. A set of x-ray lines present in the first, second and third transformations indicated the crystallization of α-Hf. The second

transformation product showed a second set of lines which were indexed on the basis of the orthorhombic Re_3B structure type as Hf_3Ni and gave the following lattice constants:

a = 0.3235 nm

b = 1.089nm

c = 0.8777nm

The difference between the samples heated to 525°C and 630°C was the relative amount of α-Hf and Hf_3Ni. While the main phase in the 525°C product was α-Hf, Hf_3Ni (a metastable phase) formed the main phase in the 630°C product. From this observation it was concluded that the crystallization of Hf_3Ni may take place by two different mechanisms, one slower than the other. Where -Hf is the only crystalline phase (when heated to 465°C) or the main crystalline phase (when heated to 525°C) it would follow that either a Ni-enriched amorphous matrix or a microcrystalline Ni-rich phase is also present which cannot give a crystalline pattern.

2. $Hf_{62}Ni_{38}$: This alloy showed a thermal effect at 535°C which is thought to be due to some atomic rearrangement in the amorphous phase or partial microcrystallization which could not give a crystalline diffraction pattern. A second transformation occurred at 590°C with a similar thermal effect to that at 535°C.

Crystallization was evidenced only at temperatures above that of the second thermal effect. Some of the x-ray lines in the crystalline pattern were indexed on the basis of a (Ti_2Ni) type structure with a lattice constant a ≈ 1.2001nm (79BUS). This cubic structure was thought to be the stable Hf_2Ni phase. However, the structure type and lattice parameter do not match those accepted for Hf_2Ni (see Table 1).

3. $Hf_{36}Ni_{64}$: A single crystallization peak is reported to occur in the DSC trace of amorphous $Hf_{36}Ni_{64}$ but remains unidentified.

4. $Hf_{11}Ni_{89}$: Two overlapping peaks are reported and not identified in the DSC trace of amorphous $Hf_{11}Ni_{89}$.

From this work it was concluded that the crystallization temperatures, T_{cr}, increased with the 3d metal concentration over a fairly large concentration range $0.2 \leq \chi \leq 0.8$ and decreased again at fairly high 3d metal concentrations, $= 0.89$. T_{cr} is expected to be proportional to the formation enthalpy, ΔH_f, of a vacancy or a hole of the size of a 3d atom, Ni (79BUS).

Crystallography

Ni-rich and Hf-rich terminal solutions: There are no lattice parameter data available on the Ni-rich and Hf-rich terminal solutions. However, the solubility ranges are very restricted and considering the atomic radii of Ni and Hf one would expect a slight increase in the Ni-lattice parameter and a slight decrease in the Hf-lattice parameter.

Ni_5Hf: This alloy has the structure type of $AuBe_5$ and contains 24 atoms per cell. The lattice parameter of Ni_5Hf was determined by 61DWI as a = 0.6683nm.

Ni_7Hf_2: The crystal structure of NI_7Hf_2 was identified by (73DAT) and found to be isotypic to Ni_7Zr_2. This phase has monoclinic structure with the lattice parameters

a = 1.2102 nm

b = 0.8191 nm

c = 0.4657 nm and

= 95.509°

Ni_3Hf: This phase was first identified by 67SVE as a $TiNi_3$-type structure but no unit cell parameters were determined. Later 78BSE1 identified two forms of Ni_3Hf with two distinct crystal structures and properties. α -Ni_3Hf is a ductile high temperature modification, stable above 1200°C, which

crystallizes with the $BaPb_3$-type structure and R3m (No 166) space group. α -Ni_3-Hf has a triply primitive hexagonal unit cell with a = 0.52787 nm and c = 1.92324 nm. The structure is described as a stacking of nine triangularly ordered, close-packed AB_3 layers. β-Ni_3Hf form, stable below 1200°C, has the lattice parameters a = 0.52822 nm and c = 2.13916 nm at room temperature. The space group of this form is $P6_3$ mmc (No 194), and the structure type is γ-Ta $(Pd,Rh)_3$ with the stacking of ten AB_3 layers in the sequence ABCBCACBCB.

$Ni_{21}Hf_8$: This phase was previously denoted as Ni_5Hf_2 by 61KIR and 67SVE. Using single crystal diffraction data 78BSE2 determined that this phase crystallizes with a triclinic unit cell in space group P1 and its true composition is Hf_8Ni_{21}. Bsenko determined the cell parameters and α, β, γ as follows

a = 0.64275 nm, α = 75.18

b = 0.80007 nm β = 68.14

c = 0.85540 nm γ = 75.61

The coordination number for each Hf atom is 15 and for the 11 non-equivalent sets of Ni atoms it varies from 12 to 13 (78BSE2).

Ni_7Hf_3: The crystal structure of this phase was originally identified by 78BSE3. This phase crystallizes in the

triclinic system and the space group P1. The structure is considered to consist of a stacking of 3 slightly puckered layers parallel to the (011) plane. The lattice parameters were determined from single crystal x-ray diffraction data and found to be:

a = 0.65138 nm and α =104.87°

b = 0.65890 nm β =104.60°

c = 0.76271 nm γ = 112.71°

$Ni_{10}Hf_7$: The crystal structure of this phase is Base-centered orthorhombic and the space group symmetry is C^{17}-C 2ca, 61KIR and 62KIR. From single crystal data the lattice dimensions were determined as:

a = 1.2275 nm

b = 0.9073 nm

c = 0.9126 nm

$Ni_{11}Hf_9$: This alloy was identified by 61KIR as a body-centered tetragonal structure and determined the lattice parameters as

a = 0.979 nm

c = 0.653 nm

The space group symmetry of this phase is 4/mI / determined from crystals having the composition of the hafnium rich phase boundaries.

NiHf: The crystal structure of NiHf was determined by 61KIR and 62KIR from crystals having the composition of the hafnium-rich phase boundary. The structure of this phase is Base-centered orthorhombic and has a space group symmetry D_{2L}^{17}-Cmcm. The lattice dimensions determined at room temperature are

$$a_o = 0.322 \text{ nm}$$

$$b_o = 0.982 \text{ nm}$$

$$c_o = 0.412 \text{ nm}$$

$NiHf_2$: This phase has a body-centered tetragonal structure with D_{4h}^{18}-14 mcm space group symmetry, 61KIR1, 62KIR1. The lattice dimensions were determined to be

$$a = 0.674 \text{ nm}$$

$$c = 0.558 \text{ nm}$$

from crystals having the composition of the Hf-rich phase boundary.

Thermodynamics

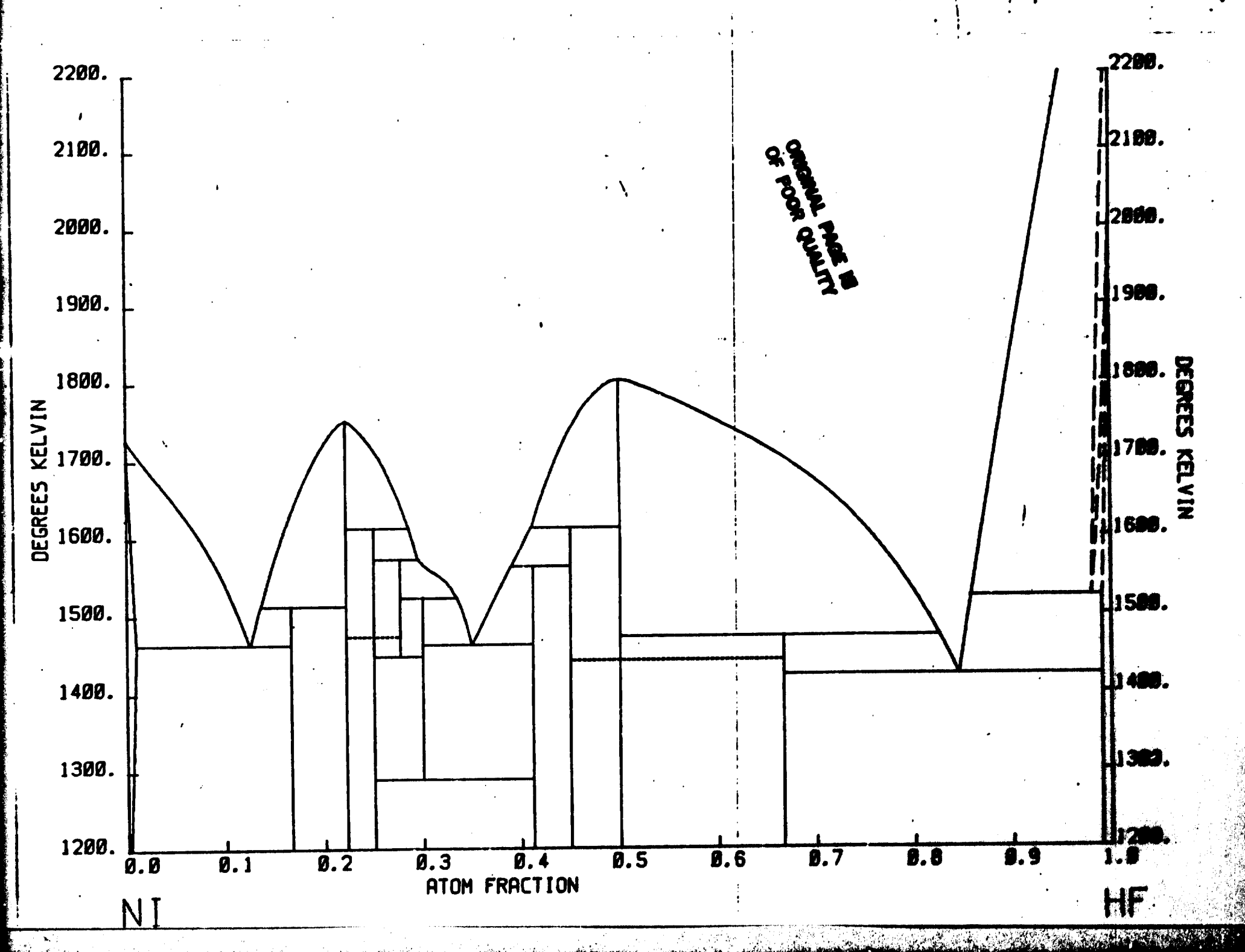
No experimental thermodynamic data is available for the Hf-Ni system. Kaufman and Nesor (73KAU) modelled this system to produce a Hf-Ni diagram which is a compromise between the data of 65ELL and 67SVE. The description used indicates large negative free energies of formation for Hf-Ni compounds, Table 2.

Table 1. Crystal Structure Data for Hf-Ni Phases

Phase	Approximate Composition at .% Hf	Pearson Symbol	Prototype	Lattice Parameters, nm a α	b β	c γ	References
Ni_5Hf	16.7	cF_{24}	$AuBe_5$	0.6683			61DWI
Ni_7Hf_2	22.2	-	-	1.2102	0.8191	0.4657	73DAT
α-Ni_3Hf	25.0	-	$BaPb_3$	0.52787 90.0°	0.52787 90.0°	1.92324 120.0°	78BSE1
β-Ni_3Hf	25.0	-	γ-Ta(Pd, Rh)$_3$	0.52822 90.0°	0.52822 90.0°	2.13916 120.0°	78BSE1
$Ni_{21}Hf_8$	27.6	-	-	0.64275 75.18°	0.80007 68.14°	0.85540 75.61°	78BSE2
Ni_7Hf_3	30.0	-	-	0.65138 104.87o	0.65890 104.60°	0.76271 112.71°	78BSE3
$Ni_{10}Hf_7$	41.2	-	-	1.2275	0.9078	0.9126	61KIR, 62KIR1
$Ni_{11}Hf_9$	45.0	-	-	0.979	-	0.653	61KIR,
NiHf	50.0	-	CrB	0.322	0.982	0.412	61KIR, 62KIR2 67SVE
$NiHf_2$	66.7	I12	$AlCu_2$	0.6743	-	0.558	61KIR 62KIR2

Table. 2 Estimated Free Energies of Formation of Some Hf-Ni Compounds (75KAU) in Cal/gat.

Compound	At. Fraction Ni	H_f (300k)	S_f (300k)
Hf_2Ni	0.333	-11,330	0.0
HfNi	0.50	-15,525	0.0
Hf_2Ni_{10}	0.588	-14,945	0.0
Hf_2Ni_5	0.714	-13,640	0.0
Hf_2Ni_7	0.778	-12,540	0.0
$HfNi_5$	0.833	-10,075	0.0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